

## REMARKS

Claims 1, 2, 16, 17, and 39-72 have been examined and stand rejected. Claims 1, 2, 16, 17, 39-41, 43-57, 71, and 72 have been amended. Claims 3-15, 18-38, 42, and 64 have been canceled. Claims 73 and 74 have been added. No new matter has been introduced. Reconsideration and allowance of Claims 1, 2, 16, 17, 39-41, 43-63, and 65-74 in view of the following remarks is respectfully requested.

### The Objection to Claims 1, 2, 16, 17, 39-48, 51-56, 71, and 72

The Examiner has objected to Claims 1, 2, 16, 17, 39-48, 51-56, 71, and 72 as reciting the phrase "for fuel cell," which, in the view of the Examiner, is non-standard English. Claims 1, 2, 16, 17, 39-41, 43-56, 71, and 72 have been amended to recite "for a fuel cell." Withdrawal of the objection is respectfully requested.

### The Rejection of Claims 1, 2, and 39-51 Under 35 U.S.C. § 102(b)

The Examiner has rejected Claims 1, 2, and 39-51 under 35 U.S.C. § 102(b) as being anticipated by Cavalca et al., U.S. Patent Application Publication No. 2001/0033960 ("Cavalca"). It is the position of the Examiner that the Cavalca reference discloses all the elements of Claims 1, 2, and 39-51, including an electrode for a fuel cell comprising a porous electron-conductive material carrying a catalyst, a proton-conductive substance arranged on surfaces of the pores of the porous electron-conductive material, and in which the pores have an average diameter of 10  $\mu$ m or less. Applicants traverse the rejection at least for the reasons set forth below.

A rejection under 35 U.S.C. § 102(b) requires that all the elements of a claim be found in a single reference. See, e.g., *In re Donahue*, 766 F.2d 531, 534 (Fed.Cir. 1985).

While not acquiescing with the Examiner's position, but in order to facilitate prosecution, Claim 1 has been amended and now recites an electrode for a fuel cell comprising a porous electron-conductive material, a catalyst, and a proton-conductive substance, wherein the pores of

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1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
206.682.8100

the porous electron-conductive material have an average diameter of 1 nm to 100 nm; the catalyst is carried in the pores of the porous electron-conductive material; the proton-conductive substance is arranged in the vicinity of the catalyst; and the proton-conductive substance is comprised of a proton-conductive substance precursor, a proton-conductive monomer or an equivalent thereto, or polymers thereof.

Support for the amendments to Claim 1 can be found in the specification as originally filed, for example, at page 4, first paragraph, which describes that the catalyst is disposed in primary pores of the electron-conductive material, and the proton-conductive substance is also disposed in the primary pores, and therefore, is "in the vicinity of" the catalyst; see also page 22, description of Fig. 1(a); and Figure 1. Support for the pore size can be found at page 5, paragraph <6>. Claims 2, and 39-51 depend from Claim 1.

Claim 1, as amended, is directed to an electrode comprising a porous electron-conductive material, in which the pores have an average diameter of 1 nm to 100 nm. It is the Examiner's position that paragraph [0133] of the Cavalca reference discloses pores that have an average diameter of about 1.05  $\mu\text{m}$  to 1.20  $\mu\text{m}$ . Applicants point out that paragraph [0133] of the Cavalca reference is describing an ionically conductive membrane, and does not describe an electrode. The Cavalca reference describes membrane electrode assembly (MEA) fuel cells as "typically made of an ionically conducting polymeric membrane sandwiched between two electronically conducting electrodes." See page 1, [0004]. The fuel cell described in the Cavalca reference is an MEA type, in which an ionically conductive membrane contacts an electronically conductive electrode to form an electrode-membrane interface. See, e.g. page 3, [0020] and [0021]. Paragraph [0133] cited by the Examiner is on page 8, under the subheading "THE MEMBRANE" [0128]. Paragraph [0132] states that "[m]embranes can be prepared with use of a microporous base material." Paragraph [0132] is followed by paragraph [0133], which states that "[a]verage pore size for the base material can be, for example, about 0.05 microns to about

0.4 microns," and further states that the pore size can be about 1.05 to about 1.20. Paragraph [0133] is clearly describing the pore size of the base material used to form the ionically conductive membrane. Paragraph [0133] does not describe the pore size of the electron conductive material. In fact, there is no description in the Cavalca reference that describes the pore size of the electron conductive material. Therefore, the Cavalca reference does not describe the pores of the porous electron-conductive material as having an average diameter of 1 nm to 100 nm, as claimed. Furthermore, the Cavalca reference does not remotely teach or suggest that the pores of the porous electron-conductive material have an average diameter of 1 nm to 100 nm, as claimed. Accordingly, the Cavalca reference does not describe all the elements of amended Claim 1, and therefore amended Claim 1 and dependent Claims 2 and 39-51 are not anticipated by, and are not obvious over, the Cavalca reference. Withdrawal of the rejection is respectfully requested.

The Rejection of Claims 16, 17, and 52-72 Under 35 U.S.C. § 102(b)

The Examiner has rejected Claims 16, 17, and 52-72 under 35 U.S.C. § 102(b) as being anticipated by Cavalca. It is the position of the Examiner that Cavalca discloses a method for producing an electrode for a fuel cell comprising the steps of (a) causing a catalyst to be carried on a porous electron-conductive material; (b) forming a proton-conductive substance on a surface, including surfaces of pores, of the porous electron-conductive material, or in the vicinity thereof; and (c) transforming the porous electron-conductive material into an assembly. Applicants traverse the rejection for at least the reasons set forth below.

*Claims 16 and 57-72*

While not acquiescing with the Examiner's position, but in order to facilitate prosecution, Claim 16 has been amended and now recites a method for producing an electrode for a fuel cell, comprising the steps of (a) causing a catalyst to be carried in the pores of a porous electron-conductive material, wherein the pores of the porous electron conductive material have

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1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
206.682.8100

an average diameter of 1 nm to 100 nm; (b) forming a proton-conductive substance in the pores of the porous electron-conductive material; and (c) transforming the porous electron-conductive material into an assembly, wherein the steps can be changeable in the order thereof, thereby forming the proton-conductive substance in the vicinity of the catalyst, which is located on the surfaces of the pores of the porous electron-conductive material. Claims 57-72 depend from Claim 16.

Support for the amendments to Claim 16 can be found in the specification as originally filed, for example, at page 4, first paragraph, which describes that the catalyst is disposed in primary pores of the electron-conductive material, and the proton-conductive substance is also disposed in the primary pores, and therefore, is "in the vicinity of" the catalyst; see also page 22, description of Fig. 1(a); and Figure 1. Support for the pore size can be found at page 5, section <6>.

As discussed supra, with respect to amended Claim 1, the Cavalca reference does not describe the pores of the porous electron-conductive material as having an average diameter of 1 nm to 100 nm, as claimed. Accordingly, the Cavalca reference does not describe all the elements of amended Claim 16, and therefore does not anticipate amended Claim 16 or dependent Claims 57-72. Withdrawal of the rejection is respectfully requested.

*Claims 17 and 52-56*

While not acquiescing with the Examiner's position, but in order to facilitate prosecution, Claims 17 and 52-56 have been amended, as indicated above with respect to Claim 16, with the only differences being the order in which the steps are performed, which was set forth in the original claims. Claims 17 and 52-56 all recite the element that the pores of the porous electron-conductive material have an average diameter of 1 nm to 100 nm.

As discussed supra with respect to amended Claim 1, the Cavalca reference does not describe the pores of the porous electron-conductive material as having an average diameter of

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1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
206.682.8100

1 nm to 100 nm, as claimed. Accordingly, the Cavalca reference does not describe all the elements of amended Claims 17 and 52-56, and therefore does not anticipate amended Claims 17 and 52-56.

The of Rejection of Claims 16, 17, and 52-72 Under 35 U.S.C. § 103(a)

The Examiner has alternatively rejected Claims 16, 17, and 52-72 under 35 U.S.C. § 103(a) as being obvious over the Cavalca reference. It is the position of the Examiner that the Cavalca reference teaches all the steps of Claims 16, 17, and 52-72, but does not explicitly disclose that the steps are changeable. However, it is the view of the Examiner that it would have been obvious to one skilled in the art that the steps of the claimed method are changeable. Applicants traverse the rejection for at least the reasons, as set forth below, that the Cavalca reference does not teach all the elements of the claimed method and the claimed method produces improved results.

Obviousness is determined by analyzing the factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966). The inquiry under *Graham* includes ascertaining the differences between the prior art and the claims at issue.

The Differences Between the Cavalca Reference and Claims 16, 17, and 52-56

As discussed supra, the Cavalca reference does not teach or remotely suggest that the pores of the porous electron-conductive material have an average diameter of 1 nm to 100 nm, as claimed. Furthermore, the Cavalca reference does not teach or remotely suggest that the proton-conductive substance is formed in the pores of the porous electron-conductive material, and therefore, the proton-conductive substance is formed in the vicinity of the catalyst, which is located at the surface of the pores of the porous electron-conductive material, as claimed.

The Cavalca reference teaches a method of preparing an electrode in which a dispersion of carbon black-platinum particles in 2-methyl alcohol is prepared, and isopropyl alcohol containing Nafion perfluorosulfonic acid is added to the dispersion and mixed with the aid of

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1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
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ultrasonic agitation. The liquid mixture is then painted onto a porous polytetrafluoroethylene electrode support film. See page 7, paragraphs [0116] and [0117] (Procedure A). As explained in Kuroki and Yamaguchi, *Journal of The Electrochemical Society*, 153(7) A1417-A1423 (2006), attached as Exhibit A, when using a conventional fabrication process in which carbon-catalyst particles are simply mixed with a perfluorosulfonic ionomer, which is the process described in Cavalca, the perfluorosulfonic ionomer added to the catalyst layer exists only in "secondary" pores, as opposed to micro-sized "primary" pores, due to the large molecular size of the perfluorosulfonic ionomer, and only the secondary pores act as reaction sites. See page A1420, second column. As explained in the specification at page 22, last sentence, to page 23, top of the page, secondary particles are formed by clustering of primary particles. Secondary pores are formed between the secondary particles. See, also, Figure 1(b).

In contrast to the electrode described in the Cavalca reference, the claimed method provides micro-structural three-phase interfaces, i.e., regions at which the "porous electron-conductive material," the "catalyst," and the "proton-conductive substance," are contacted with each other. See specification at page 4, lines 1-21. Micro-structural three-phase interfaces in pores having an average diameter of 1 nm to 100 nm, as claimed, cannot be produced by Procedure A described in the Cavalca reference. Accordingly, the Cavalca reference does not remotely teach or suggest the method recited in Claim 16, and therefore, the Examiner has not established a *prima facie* case of obviousness.

#### The Claimed Method Results in Improved Properties

Non-obviousness can be shown by providing evidence that the claimed invention yields unexpectedly improved properties or properties not present in the prior art. See M.P.E.P. § 2145.

Applicants have found that the micro-structural three-phase interfaces produced by the claimed method provide a higher specific surface area of the porous electron-conductive material, resulting in an enhanced effective electrode for a fuel cell. See page 4, lines 16-21.

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1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
206.682.8100

As discussed above, because the Cavalca reference does not remotely teach or suggest all the elements of Claims 16, 17, and 52-56, and because the claimed method produces an electrode for a fuel cell with improved properties, Claims 16, 17, and 52-56 are not obvious over the Cavalca reference. Withdrawal of the rejection is respectfully requested.

New Claims 73 and 74

Claims 73 and 74 have been added.

Claim 73 recites a method for producing an electrode for a fuel cell, comprising the steps of (a) causing a catalyst to be carried in the pores of a porous electron-conductive material; (b) binding a proton-conductive substance in the pores of the porous electron-conductive material; and (c) transforming the porous electron-conductive material into an assembly, wherein the steps can be changeable in the order thereof, thereby forming the proton-conductive substance in the vicinity of the catalyst, which is located on the surfaces of the pores of the porous electron-conductive material.

Claim 74 recites an electrode for a fuel cell comprising a porous electron-conductive material, a catalyst and a proton-conductive substance, wherein the catalyst is carried in the pores of the porous electron-conductive material, the proton-conductive substance is comprised of a proton-conductive substance precursor, a proton-conductive monomer or an equivalent thereto, or polymers thereof, and the proton-conductive substance is bound to the porous electron-conductive material in the vicinity of the catalyst.

Support for Claims 73 and 74 can be found in the specification as originally filed, for example, at page 4, first paragraph, which describes that the catalyst is disposed in primary pores of the electron-conductive material, and the proton-conductive substance is also disposed in the primary pores, and therefore, is "in the vicinity of" the catalyst; see also page 22, description of Fig. 1(a); and Figure 1. Support for the element that the proton-conductive substance is bound in

the pores of the porous electron-conductive material and, therefore, in the vicinity of the catalyst can be found at page 6, paragraph <8>.

Claims 73 and 74 are not anticipated by, and are not obvious over, the Cavalca reference for at least the reasons discussed below.

#### The Differences Between Claims 73 and 74 and the Cavalca Reference

As discussed supra, the Cavalca reference does not teach or remotely suggest that the proton-conductive substance is formed in the pores of the porous electron-conductive material, and therefore, that the proton-conductive substance is formed in the vicinity of the catalyst, which is located at the surface of the pores of the porous electron-conductive material, as claimed. Furthermore, the Cavalca reference also does not remotely teach or suggest that the proton-conductive substance is bound in the pores of the porous electron-conductive material, as claimed.

The Examiner cites paragraph [0141] of the Cavalca reference as describing that one end of the proton-conductive substance is bound to the surface of the porous electron-conductive material. Paragraph [0141] is under the heading "COMBINING ELECTRODE AND MEMBRANE; THE INTERFACIAL REGION" [0139]. Paragraph [0141] states the following: "Also, ion conductive polymer can be at the surface of the electrode, before the electrode surface is contacted with the ion conductive polymer of the membrane. Merger or fusion of the two ion conductive polymers can occur" (emphasis added). Therefore, the Cavalca reference does not teach that the proton-conductive substance is bound in the pores of the porous electron-conductive material, as claimed. Furthermore, the chemical vapor deposition cited by the Examiner in paragraph [0158] of the Cavalca reference refers to deposition of a second catalytically active metal in the interfacial region. It does not refer to deposition of a proton-conductive substance to the porous electron-conductive material in the vicinity of the catalyst, as claimed.

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1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
206.682.8100



Under the M.P.E.P. § 2141.03, the teachings of the reference must be considered as a whole. See, also, e.g., *Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve, Inc.*, 230 U.S.P.Q. 416, 419 (Fed. Cir. 1986) ("[i]t is impermissible within the framework of section 103 to pick and choose from any one reference only so much of it as will support a given position, to the exclusion of other parts necessary to the full appreciation of what such reference fairly suggests to one of ordinary skill in the art.") Applicants respectfully submit that paragraphs [0141] and [0158] cited by the Examiner to support his position are taken out of context and do not remotely teach or suggest that the proton-conductive substance is bound in the pores of the porous electron-conductive material, in the vicinity of the catalyst, as claimed.

#### The Claimed Method Results in Improved Properties

As discussed supra, the micro-structural three-phase interfaces produced by the claimed method provide a higher specific surface area of the porous electron-conductive material, resulting in an enhanced effective electrode for a fuel cell. Furthermore, binding the proton-conductive substance to the porous electron-conductive material prevents the proton-conductive substance from leaching out of the electrode when the electrode is contacted with water during the operation of the fuel cell. See, e.g., specification at pages 11-12, paragraph <43>. If the proton-conductive substance is leached out during operation of the fuel cell, then the performance of the fuel cell will be reduced. Therefore, prevention of leaching of the proton-conductive substance provides an enhanced effective electrode for a fuel cell.

Accordingly, for the reasons discussed above, Claims 73 and 74 are not anticipated by and are not obvious over the Calvaca reference.

#### Conclusion

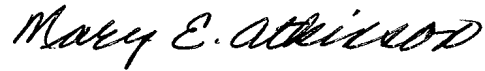
Applicants believe that Claims 1, 2, 16, 17, 39-41, 43-63, and 65-74 are in condition for allowance. Reconsideration and favorable action is requested. If any issues remain that may be

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CHRISTENSEN O'CONNOR JOHNSON KINDNESS<sup>PLLC</sup>  
1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
206.682.8100

expeditiously addressed in a telephone interview, the Examiner is encouraged to telephone applicants' attorney at 206.695.1795.

Respectfully submitted,

CHRISTENSEN O'CONNOR  
JOHNSON KINDNESS<sup>PLLC</sup>

A handwritten signature in black ink that reads "Mary E. Atkinson". The signature is written in a cursive, flowing style.

Mary E. Atkinson  
Registration No. 48,767  
Direct Dial No. 206.695.1795

MEA:mea

LAW OFFICES OF  
CHRISTENSEN O'CONNOR JOHNSON KINDNESS<sup>PLLC</sup>  
1420 Fifth Avenue  
Suite 2800  
Seattle, Washington 98101  
206.682.8100



# Nanoscale Morphological Control of Anode Electrodes by Grafting of Methylsulfonic Acid Groups onto Platinum–Ruthenium-Supported Carbon Blacks

Hidenori Kuroki and Takeo Yamaguchi<sup>\*,‡</sup>

Department of Chemical System Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

An increase in catalyst utilization in direct methanol fuel cells (DMFCs) is necessary to improve performance and reduce costs. We propose an electrode fabrication method, based on the process of grafting a proton-conducting agent onto catalyst-supported carbons before the conventional electrode fabrication process where catalyst-supported carbons are simply mixed with the perfluorosulfonic ionomer. In this study, methylsulfonic acid groups ( $-\text{CH}_2\text{SO}_3\text{H}$ ) as proton-conducting agents have been successfully introduced to the pores of catalyst-supported carbons. We found that the chemical connections between the grafted methylsulfonic acid groups and the surface of catalyst-supported carbons were stable up to around  $380^\circ\text{C}$ . Furthermore, by morphological analysis, we found that the grafted methylsulfonic acid groups were homogeneously introduced into both the primary and the secondary pores, and produced no significant structural change in the secondary pore that could affect the mass transfer process. The DMFC performance of the membrane electrode assembly (MEA) made using our grafting method was superior to that of an MEA made using the conventional method. A maximum power density of  $87 \text{ mW cm}^{-2}$  was obtained by using grafted catalyst-supported carbons at an anode electrode in the DMFC in the low Pt–Ru loading amount of ca.  $0.7 \text{ mg cm}^{-2}$  (Pt loading amount: ca.  $0.5 \text{ mg cm}^{-2}$ ) at  $50^\circ\text{C}$  under atmospheric pressure.  
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$\text{H}_2/\text{O}_2$  polymer electrolyte fuel cells (PEFCs) have received much attention on account of their attractive properties as power sources for portable, automobile, and home electricity applications. In particular, liquid-fed direct methanol fuel cells (DMFCs), which are a type of PEFC, are also promising as an alternative power source for the next generation of mobile devices and small stationary power applications because of their high energy density, the ease of fuel storage and delivery, and the ability to operate at, or near, ambient temperatures. However, as  $\text{H}_2/\text{O}_2$ -PEFCs and liquid-fed DMFCs require a platinum catalyst as an active material for electrodes, the high cost of that catalyst has restricted their commercialization.<sup>1</sup>

Therefore, several studies have focused on lowering the platinum loading in the PEFC electrodes.<sup>2–10</sup> The underlying concept of these studies is to enhance catalyst utilization in the electrode by extending the three-phase boundary. The three-phase boundary structure is shown in Fig. 1. Note that only catalyst particles that keep contact with both electrolyte and reactant substance are electrochemically active. Although several efforts have been made to optimize this three-phase boundary structure, and various methods for producing it have been widely reported,<sup>2,11–16</sup> a substantial amount of platinum in the catalyst layer may still not be fully utilized.

One reasonable explanation for low platinum utilization was presented by Uchida et al.,<sup>17</sup> who studied the microstructure of the catalyst layer. In the general process of catalyst fabrication, nanometer-sized platinum catalysts were dispersed on the surface of 30–40 nm-sized carbon substrates to increase the platinum catalyst surface area. However, these small carbon particles tend to agglomerate via intermolecular interaction between their surfaces, thus the platinum inside the agglomerated carbon structure cannot be utilized in electrochemical reactions. This is because the perfluorosulfonate ionomer (ca.  $0.04 \mu\text{m}$ ), which is generally added to the catalyst layer as a proton-conducting agent during the electrode fabrication process, cannot penetrate into the smaller pores ( $< \text{ca. } 0.04 \mu\text{m}$ ) of the agglomerated carbon structure.

Here we propose an electrode fabrication method to achieve an ideal structure of the reaction field in the catalyst layer. In this method, the electrolyte groups are grafted onto catalyst-supported carbons before the conventional electrode fabrication process in which the catalyst-supported carbons are simply mixed with the per-

fluorosulfonic ionomer. Due to its small molecular size, the graft electrolyte groups are able to penetrate into the small pores of the agglomerated carbon structure. This ensures that most of the resulting protons at the catalyst surface can access the graft electrolyte groups, easing the proton conducting process at the three-phase boundary structure; using the conventional method, however, it is likely that the perfluorosulfonate ionomer is not uniformly distributed throughout the catalyst layer and the catalyst particles not in contact with the electrolyte groups cannot be utilized for the electrochemical reactions.

As reported previously by Mizuhata et al.,<sup>18</sup> we performed a graft polymerization of electrolyte polymer from the monomer (acrylamide tertiary butyl sulfonic acid: ATBS, Toagosei Co. Ltd.) solution onto catalyst-supported carbons and succeeded in introducing graft electrolyte polymer into the smaller pores of the agglomerated carbon structure. Using this method, we found that the electrochemically active area in the catalyst was increased severalfold at the cathode in the  $\text{H}_2/\text{O}_2$ -PEFC and that the performance obtained was slightly higher, compared with the case when the conventional method was used. We first presumed that higher amounts of graft electrolyte polymer would increase the number of platinum particles effectively used in the electrochemical reaction and superior fuel cell performances could be obtained. The experimental results indicated that the introduction of higher amounts of graft electrolyte

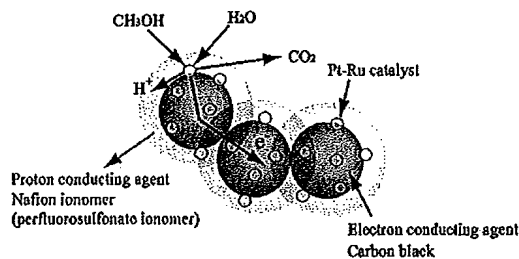
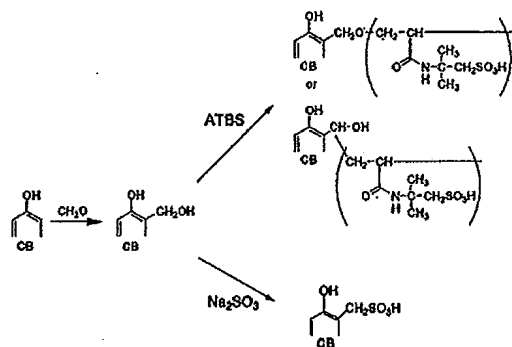


Figure 1. Schematic illustration of the three-phase boundary structure. Nanometer-sized platinum–ruthenium (Pt–Ru) catalysts are dispersed on each 30–40 nm sized carbon black surface, and the carbon black particles are covered with Nafion ionomers. The three-phase boundary structure ensures that catalyst particles keep contact with Nafion ionomer and carbon black, which is a conducting agent for proton and electron, respectively.

<sup>\*</sup> Electrochemical Society Active Member.  
<sup>‡</sup> E-mail: yamag@chemsys.t.u-tokyo.ac.jp

polymer resulted in the effective utilization of the catalyst into the primary pores as reaction sites, however, and it also resulted in inferior cell performance in the high current-density range. It has been reported<sup>2,19,23</sup> that there is a correlation between cell performance in the high current density range and the mass transport process in an electrode. If the excess grafted electrolyte polymer was filled in the pores in the catalyst layer, mass transport problems would be caused by retarding access of the reactant gas to the active sites, which can be the reason for the extreme degradation of cell performance in high current density range. Therefore, we suggested that to obtain a higher cell performance with a low catalyst-loading amount, the carbon structure in the catalyst layer was necessary to increase the catalyst utilization as reaction sites, especially in the primary pores, and furthermore maintain adequate mass transfer. Recently, other studies such as the introduction of proton-conducting agents in the microstructure in the catalyst layer have also been reported.<sup>24,26</sup> However, in the case of these studies, a link between morphological analysis and fuel-cell performance was not clarified, and the optimal microstructure in the catalyst layer with both high catalyst utilization at reaction sites and higher cell performance with adequate mass transfer also have not yet been achieved.

For the above-mentioned reasons, to obtain a higher cell performance with a low catalyst-loading, it is necessary that a shorter grafted chain as the proton-conducting agent than ATBS polymer be introduced into pores of agglomerated carbons. Therefore, as indicated in the following reaction scheme (Scheme 1), grafting of



Scheme 1. Comparison of reaction schemes for grafting of ATBS polymer and methylsulfonic acid groups onto catalyst-supported carbons

methylsulfonic acid groups ( $-\text{CH}_2\text{SO}_3\text{H}$ ) onto catalyst-supported carbons was performed at the anode electrode in a DMFC, based on the concept of our new electrode fabrication method.

The concept is shown in Fig. 2. In this study, this grafting method was applied to anode electrodes in a DMFC because the main loss in DMFC results from the methanol oxidative reaction at an anode electrode due to the slower reaction rate of the methanol oxidation. However, grafting of methylsulfonic acid groups onto fuel-cell catalyst-supported carbons has never before been performed. It has been reported<sup>27,28</sup> that the methylsulfonic acid group was introduced onto phenol by treatment with formaldehyde and sodium sulfite (or sodium bisulfite) and it is also generally known that the reactivity of phenolic hydroxyl groups on catalyst-supported carbons is the same as the hydroxyl group on phenol. Therefore, we expected that the method for phenol could be applied to phenolic hydroxyl groups on catalyst-supported carbons. Moreover, it was expected that grafted methylsulfonic acid groups had better stability by being fixed directly onto surfaces of the catalyst-supported carbons by the grafting method and, by grafting methylsulfonic acid groups inside the pores of the catalyst layer, it was also expected

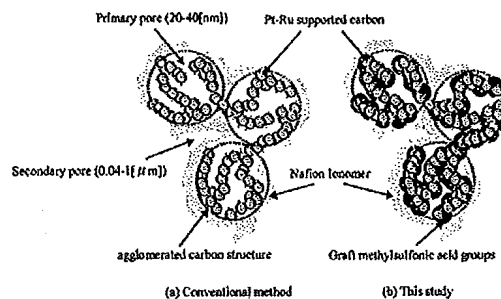
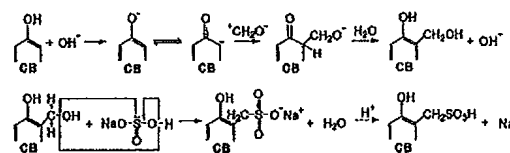


Figure 2. Schematic illustration of the internal structure of the catalyst layer. (a) Catalyst layer made by nongrafted Pt-Ru/Ketjenblack. (b) Catalyst layer made by grafted Pt-Ru/Ketjenblack. Nanometer-sized Pt-Ru catalysts are dispersed on each 30–40 nm sized carbon black surface, and the carbon black particles are agglomerated. Nafion ionomers are partly covered on the agglomerated structure.

that mass transport problems would not occur, because the chain length of the grafted methylsulfonic acid groups is far shorter than that of ATBS polymer. Thus, the catalyst active area will be increased at an anode electrode and a higher cell performance in the DMFC will be obtained, compared with the conventional method. We evaluated our concept by investigating the morphology of the grafted catalyst-supported carbons and examined the cell performances in DMFCs. Moreover, we also discuss the effects of the grafted methylsulfonic acid groups on catalyst-supported carbons.

## Experimental

**Grafting on catalyst-supported carbons.**—As mentioned above, we attempted the introduction of methylsulfonic acid groups onto the catalyst-supported carbons by the same method as used for phenol.<sup>27,28</sup> The reaction scheme (Scheme 2) is as follows.



Scheme 2. The detailed reaction scheme for grafting of methylsulfonic acid groups onto catalyst-supported carbons

We used Ketjenblack-supported 32.5 wt % platinum–16.9 wt % ruthenium (Tanaka Kikinzoku Kogo, Pt-Ru/Ketjenblack) as catalyst-supported carbon. Grafting of methylsulfonic acid groups onto catalyst-supported carbon was achieved as follows. In a flask, 3.0 g of catalyst-supported carbon was added to 50 mL of pure water. Subsequently, 0.59 g of a 36–38% formaldehyde aqueous solution and 3.44 g of sodium sulfite were added. The mixture was heated at 110°C with stirring and refluxing solvent. After a 24 h reaction time, the resulting catalyst-supported carbon was filtered and protonated with 1 N hydrochloric acid aqueous solution. Finally, after ion exchanging the grafted catalyst-supported carbon was extracted with pure water using a Soxhlet apparatus to fully remove nonreacted substances.

The grafted methylsulfonic acid groups on the catalyst-supported carbons were confirmed by Fourier transform infrared (FTIR) spectroscopy using a Magna IR 560 (Nicolet) spectrophotometer, by thermogravimetry-mass spectrometry (TG-MS) using a TGA 7 (Per-

kin Elmer) and Thermostat (Perkin Elmer), and by CHNS elemental analysis using a PE 2400 II (Perkin Elmer). Wafers of KBr containing a small amount of sample were used to obtain the transmission FTIR spectra in the range of 400–1400  $\text{cm}^{-1}$ . TG-MS analysis was carried out on the TGA 7 thermobalance coupled to a Thermostat mass spectrometer through a transfer line connected to a vacuum pump and heated at 200°C. The TGA 7 was operated from 30°C to 600°C with a heating rate of 10°C  $\text{min}^{-1}$  under a continuous flow of  $\text{N}_2$  (100  $\text{mL min}^{-1}$ ). The primary pore size distribution and the specific pore volume of the grafted or nongrafted catalyst-supported carbons were determined by mercury intrusion porosimetry using an Auto Pore 9520 (Micromeritics). The secondary pore size distribution and the specific pore volume of the anode electrodes made by the grafted or nongrafted catalyst-supported carbons were determined as through pores of the anode electrodes by a bubble point test using Perm-Porometer (PMI). These two parameters of the primary and secondary pores are important to discuss the three-phase boundary structure.

**Fabrication process of membrane-electrode assemblies (MEAs).**—The electrodes consisted of a backing layer, which also acted as a current collector, a gas diffusion layer, and a catalyst layer. The catalysts used at the anode and cathode electrodes were Pt–Ru/Ketjenblack (32.5 wt % platinum–16.9 wt % ruthenium on Ketjenblack, Tanaka Kikinzoku Kogyo) and Pt/Ketjenblack (55.3 wt % platinum on Ketjenblack, Tanaka Kikinzoku Kogyo), respectively.

For DMFCs, the loss at an anode is higher than that at a cathode. Most of the loss at an anode is due to the high activation overpotential of the methanol oxidation reaction. Thus, grafted Pt–Ru/Ketjenblack was used to fabricate an anode catalyst layer. The same anode layer made with nongrafted Pt–Ru/Ketjenblack was also prepared for comparison. For the cathode, nongrafted Pt/Ketjenblack was used.

The anode electrodes were fabricated as follows. A gas diffusion layer was formed on non-Teflonized carbon paper (ElectroChem, Inc.). The inks for the catalyst layers were prepared from the grafted or nongrafted Pt–Ru/Ketjenblack and Nafion solution (Aldrich, 5 wt % in 15–20 % water/low aliphatic alcohols) with pure water as the solvent. The mixing ratio of Pt–Ru/Ketjenblack and Nafion was fixed at 12:5 by weight in the dry state. The resulting inks were spread over the gas diffusion layer. Subsequently, the cathode electrodes were fabricated as follows. First, the gas diffusion layer was formed on Teflonized carbon paper. The inks for the catalyst layers were prepared from the nongrafted Pt/Ketjenblack, the Nafion solution, and the PTFE suspension (Aldrich, 60 wt % dispersion in water) with water as the solvent. The weight ratio of Pt/Ketjenblack, Nafion, and PTFE was fixed at 60:25:15 in the dry state. The resulting inks were spread over the gas diffusion layer. The Pt loading amount in the catalyst layer of the cathode electrodes was fixed at ca. 1.0  $\text{mg cm}^{-2}$ .

The MEAs were fabricated as follows. Pretreated Nafion 112 membrane was adopted as a polymer electrolyte membrane and sandwiched between the two square-shaped pieces (5  $\text{cm}^2$ ) from the anode and cathode, prepared using the method above, and hot-pressed at 130°C and 2 MPa for 1 min.

**DMFC experiments.**—The MEAs obtained were characterized in a 5  $\text{cm}^2$  single cell (ElectroChem, Inc.) at 50°C under atmospheric pressure. The fuel was fed to an anode at a flow rate of 10  $\text{mL min}^{-1}$  for 2.5  $\text{mol L}^{-1}$  methanol aqueous solution and the reactant gas to a cathode at a flow rate of 1000  $\text{mL min}^{-1}$  for  $\text{O}_2$  gas. In this study, we focused on the three-phase boundary structure as the electrochemically active area at anode electrodes. Therefore, we performed cell performance tests in high flow rate not including the effect such as flooding, especially of cathode electrodes. Measurements of cell potential as a function of current density were made galvanostatically using an electronic load (HJ-SM8, Battery Charge/Discharge Unit, Hokuto Denko Co., Ltd).

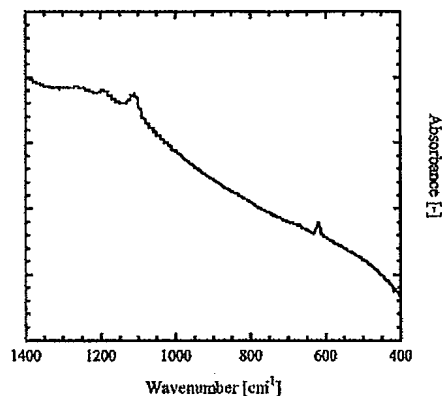


Figure 3. FTIR spectra of sample 1. The line shows the difference in the FTIR spectrum from before and after grafting methylsulfonic acid groups onto Pt–Ru/Ketjenblack. The grafting condition is the same as for sample 1 shown in Table I.

## Results and Discussion

**Preparation of grafted catalyst-supported carbons.**—The grafting of methylsulfonic acid groups was performed under various concentrations of reactants. The different FTIR spectra from before and after grafting of methylsulfonic acid groups onto Pt–Ru/Ketjenblack are shown in Fig. 3. There are two absorption bands near 620 and 1100  $\text{cm}^{-1}$ , which can be assigned to an SO stretching vibration and an  $\text{SO}_2$  symmetric stretching vibration, respectively. These absorption bands must correspond to grafted methylsulfonic acid groups.

Figure 4 shows the results of TG-MS analysis. Peaks for molecular mass 48 and 64 were confirmed around 380°C. Molecular mass 48 and 64 correspond to SO and  $\text{SO}_2$ , the peaks of SO and  $\text{SO}_2$  being derived from the grafted methylsulfonic acid groups.

Therefore, grafted methylsulfonic acid groups were successfully introduced to the pores of Pt–Ru/Ketjenblack using our technique, and the chemical connection between grafted methylsulfonic acid groups and the surface of catalyst-supported carbons was considered to be stable up to around 380°C.

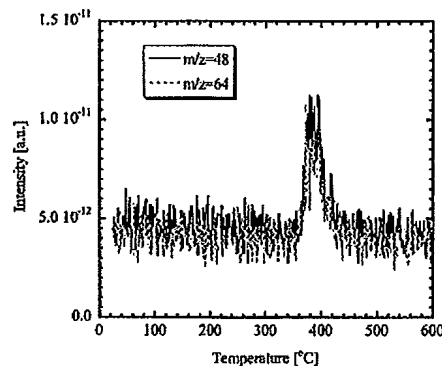


Figure 4. TG-MS analysis of sample 3. The unbroken black line shows the intense mass signal of  $m/z$  48 corresponding to SO. The dashed gray line shows the intense mass signal of  $m/z$  64 corresponding to  $\text{SO}_2$ . The grafting condition is the same as for sample 3 shown in Table I.

Table I. Graft methylsulfonic acid groups onto Pt-Ru/Ketjenblack.

	Grafting condition <sup>a</sup>			Results of evaluation	
	HCHO conc./ g-cat <sup>b</sup> (mmol/g-cat)	Na <sub>2</sub> SO <sub>3</sub> conc./ g-cat <sup>b</sup> (mmol/g-cat)	Graft methylsulfonic acid group content <sup>c</sup> (vol %)	Primary pore volume <sup>d</sup> (cm <sup>3</sup> /g-cat)	Filling ratio (%)
Pt-Ru/Ketjenblack	—	—	—	0.426	—
Sample 1	2.4	9.1	10.7	0.374	13.0
Sample 2	1.4	0.8	9.3	0.386	9.6
Sample 3	24.8	9.1	8.9	0.391	8.0
Sample 4	150.8	75.0	8.4	0.393	6.9

<sup>a</sup> Grafting conditions were fixed as follows: 3.0 g Pt-Ru/Ketjenblack having phenolic hydroxyl groups, 24 h and 110°C.

<sup>b</sup> The concentration of reactants is expressed per the weight of catalyst-supported carbon black.

<sup>c</sup> Grafted methylsulfonic acid group content in the samples was determined from elemental analysis.

<sup>d</sup> Primary pores are those in the range 0.02–0.04  $\mu\text{m}$ . Pore volume is expressed per weight of Pt-Ru/Ketjenblack in the sample.

<sup>e</sup> Filling ratios of methylsulfonic acid groups in the primary pores were determined by the decrease in the primary pore volume.

Table I shows the results of elemental analysis. Because Pt-Ru/Ketjenblack contains no sulfur compounds before grafting of methylsulfonic acid groups, grafted methylsulfonic acid group content in the sample is calculated by the difference in the weight percentage of sulfur before and after grafting of methylsulfonic acid groups. From Table I, as for Pt-Ru/Ketjenblack, the volume percentage per the primary pore volume was almost constant at a value of ca. 10 vol %, even if the concentrations of reactants were varied, because the content of phenolic hydroxyl groups on the catalyst-supported carbons was constant. It can be concluded that grafted methylsulfonic acid groups can be introduced onto Pt-Ru/Ketjenblack up to ca. 10 vol %.

**Morphology analysis of the grafted catalyst-supported carbons.**— We have reported<sup>16</sup> that a catalyst layer has two distinctive pore distributions with a boundary of about 0.04  $\mu\text{m}$ , the smaller pores (primary pores) from 0.02 to 0.04  $\mu\text{m}$  were identified with the space between the primary particles inside the agglomerated carbons, and the larger pores (secondary pores) were those between the agglomerated carbons.

Figure 5 shows the results of the mercury porosimeter analysis for primary pore size distribution of the Pt-Ru/Ketjenblack before

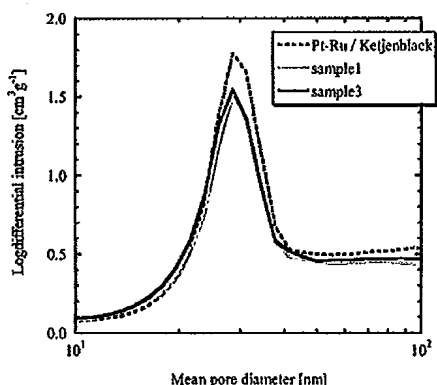


Figure 5. Primary pore size distribution curves for the Pt-Ru/Ketjenblack by mercury porosimeter analysis. The dashed black line shows the pore size distribution curve for the Pt-Ru/Ketjenblack without grafted methylsulfonic acid groups. The unbroken black and gray lines show the pore size distribution curve for the Pt-Ru/Ketjenblack after grafting methylsulfonic acid groups. The grafting condition is the same as for samples 1 and 3 shown in Table I.

and after grafting of methylsulfonic acid groups. The log differential intrusion is expressed per weight of Pt-Ru/Ketjenblack in the sample. The weight of Pt-Ru/Ketjenblack was determined from elemental analysis. From Fig. 5, there is a distinctive peak in the pore size distribution at 0.02–0.04  $\mu\text{m}$  as the primary pores. It is evident that grafted methylsulfonic acid groups in the sample decrease the primary pore volume. Furthermore, Table I shows that the filling ratio of methylsulfonic acid groups in the primary pores obtained by mercury porosimeter analysis have a similar tendency to the volume percentage per the primary pore volume, which is calculated from the results of elemental analysis. The above results suggest that methylsulfonic acid groups were homogeneously introduced into both the primary and the secondary pores using our technique.

The perfluorosulfonic ionomer added to the catalyst layer exists only in the secondary pores, and only the secondary pores act as reaction sites when using the conventional fabrication process where catalyst-supported carbons are simply mixed with the perfluorosulfonic ionomer. However, we performed grafting of methylsulfonic acid groups onto catalyst-supported carbons before the conventional fabrication process to prepare the three-phase boundary structure in the catalyst layer, because the small size reactants seem to be able to penetrate into the primary pores, in contrast to the perfluorosulfonic ionomer, due to its large molecular size. Therefore, the effective utilization of the catalyst as reaction sites in the primary pores was expected by using our nanometer-sized control technique.

Moreover, the negative charge ( $\text{SO}_3^-$ ) was added onto the surfaces of carbon particles by grafting of methylsulfonic acid groups. We assumed the charge repulsion between carbon surfaces can reduce the tendency of an agglomeration of carbon particles because an agglomeration of carbon particles depends on intermolecular interaction between carbon surfaces. We performed the precipitation test using aqueous mixture of grafted or nongrafted Pt-Ru/Ketjenblack, and found the dispersion of grafted Pt-Ru/Ketjenblack was a little higher than that of nongrafted Pt-Ru/Ketjenblack. However, the intermolecular interaction force between carbon surfaces seems to be stronger than the charge repulsion force by grafted methylsulfonic acid groups, because the primary pore size was not changed after grafting of methylsulfonic acid groups.

Subsequently, Fig. 6 shows the results of the bubble point tests for secondary pore size distribution of the anode electrodes made by grafted or nongrafted Pt-Ru/Ketjenblack. As indicated in Fig. 6, there are several peaks in the pore size distribution at 0.1–1  $\mu\text{m}$  as the secondary pores and there was no significant change in secondary pore size distribution of the anode electrode made by grafted catalyst-supported carbons, compared with that of the anode electrode made by nongrafted catalyst-supported carbons. Therefore, we presumed that, as the secondary pores have an effect on the mass transfer process, grafted methylsulfonic acid groups inside the pores of the catalyst layer do not cause additional mass transport problems

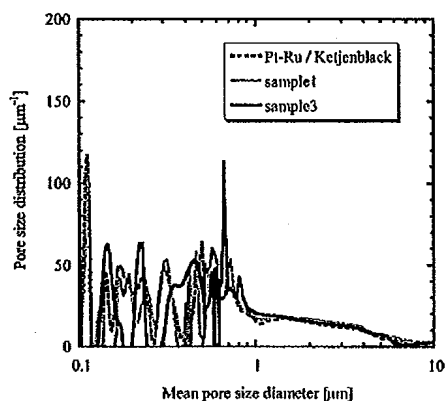


Figure 6. Secondary pore size distribution curves for the anode electrodes using the bubble point test. The dashed black line shows the pore size distribution curve for the anode electrode made by nongrafted Pt-Ru/Ketjenblack. The unbroken black and gray lines show the pore size distribution curve for the anode electrode made by grafted Pt-Ru/Ketjenblack. The grafting condition is the same as for samples 1 and 3 shown in Table I.

in the fuel cell tests in the high current-density range. As structural factors of secondary pores need not be considered, we presumed that it is possible to discuss the effects of grafted methylsulfonic acid groups on catalyst-supported carbons by comparing cell performance of grafted and nongrafted Pt-Ru/Ketjenblack.

**Fuel cell performance.**—Figure 7 compares the MEA using the anode electrode made by the conventional method (by nongrafted Pt-Ru/Ketjenblack) and the MEA using the anode electrode made by grafted Pt-Ru/Ketjenblack (sample 1) in terms of current-voltage (Fig. 7a) and current-power (Fig. 7b). The Pt-Ru loading amount at both anode electrodes was ca.  $1.0 \text{ mg cm}^{-2}$  (Pt loading amount: ca.  $0.7 \text{ mg cm}^{-2}$ ). As indicated in Fig. 7, the cell performance of the MEA made by grafted Pt-Ru/Ketjenblack was superior to that of the MEA made by nongrafted Pt-Ru/Ketjenblack. The maximum power densities were 90 and  $74 \text{ mW cm}^{-2}$  for the MEAs made by grafted and nongrafted Pt-Ru/Ketjenblack, respectively.

Subsequently, the Pt-Ru loading amount at both anode electrodes was changed to ca.  $2.0 \text{ mg cm}^{-2}$  without changing other conditions and the cell performance of the MEAs was also compared by examining current-voltage (Fig. 8a) and current-power (Fig. 8b). The MEAs were made by nongrafted and grafted Pt-Ru/Ketjenblack. From Fig. 8, the higher cell performance was obtained by using the MEA made by the grafted Pt-Ru/Ketjenblack as well as the case when the Pt-Ru loading amount at both anode electrodes was ca.  $1.0 \text{ mg cm}^{-2}$ .

We made comparisons for the low, medium and high current-density range in Fig. 7a and 8a. In the medium and high current-density range, the rate-determining step is generally the proton conduction process and the mass transfer process, respectively. From Fig. 7a and 8a the increase of the cell performances was constant or a little larger in the medium current-density range than in the low current-density range by using the MEA made by the grafted Pt-Ru/Ketjenblack. Therefore, we found that the anode electrode made by grafted Pt-Ru/Ketjenblack could be advantageous for the proton conduction process, compared with nongrafted Pt-Ru/Ketjenblack.

Moreover, Fig. 7a and 8a in the high current-density range show that the extreme performance degradation of the cells was not observed by using the MEA made by the grafted Pt-Ru/Ketjenblack. Therefore, we found that by introduction of grafted methylsulfonic acid groups into the pores of the catalyst layer, mass transport prob-

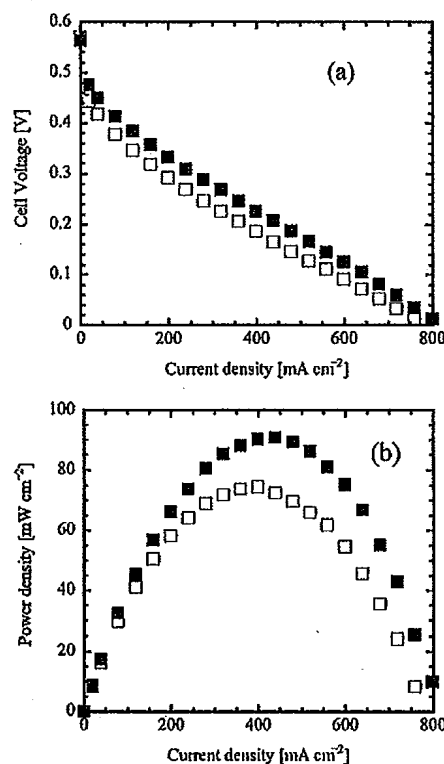


Figure 7. (a) Current-voltage and (b) current-power curves of the MEA made by nongrafted Pt-Ru/Ketjenblack ( $\square$ ) and the MEA made by grafted Pt-Ru/Ketjenblack ( $\blacksquare$ ). The grafting condition is the same as for sample 1 shown in Table I. Operating conditions: cell temperature  $50^\circ\text{C}$ ; atmospheric pressure; fuel  $2.5 \text{ mol L}^{-1}$  methanol solution; anode Pt-Ru loading amount ca.  $1.0 \text{ mg cm}^{-2}$ .

lems were not caused at an anode electrode in the DMFC, in accordance with our concept, because the chain length of the grafted methylsulfonic acid groups was much shorter than that of ATBS polymer.

Figure 9 presents the cell performance of Fig. 7a and 8a in the low current-density range ( $0\text{--}100 \text{ mA cm}^{-2}$ ). The reaction rate of methanol oxidation is generally the rate-determining step in the low current-density range. Figure 9 shows clearly that the cell performance in the low current-density range using the MEA made by the grafted Pt-Ru/Ketjenblack was increased by 30–40 mV compared with the nongrafted Pt-Ru/Ketjenblack in both case of the Pt-Ru loading amount ca.  $1.0 \text{ mg cm}^{-2}$  and ca.  $2.0 \text{ mg cm}^{-2}$ . It was therefore reasonable to conclude that the higher cell performance by the grafted Pt-Ru/Ketjenblack in the low current-density range mainly resulted from the increase of the three-phase boundary reaction area, especially in the primary pores. The increase in three-phase boundary as the electrochemically active area was accompanied by enhancement of the methanol oxidation reaction rate. Furthermore, Fig. 9 also shows that the cell performance by using the MEA made by the grafted Pt-Ru/Ketjenblack, in which the Pt-Ru loading amount at the anode electrode was ca.  $1.0 \text{ mg cm}^{-2}$ , was almost equal to the cell performance by using the MEA made by the nongrafted Pt-Ru/Ketjenblack, in which the Pt-Ru loading amount at the anode electrode was ca.  $2.0 \text{ mg cm}^{-2}$ , in the low current-density

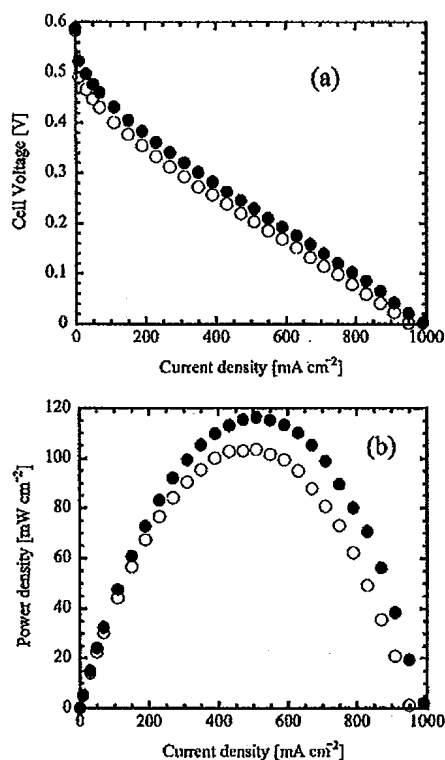


Figure 8. (a) Current-voltage and (b) current-power curves of the MEA made by nongrafted Pt-Ru/Ketjenblack (O) and MBA made by grafted Pt-Ru/Ketjenblack (●). The grafting condition is the same as for sample 1 shown in Table I. Operating conditions: cell temperature 50°C; atmospheric pressure; fuel 2.5 mol L<sup>-1</sup> methanol solution; anode Pt-Ru loading amount ca. 2.0 mg cm<sup>-2</sup>.

range. Therefore, we found that to achieve this significant increase of 30–40 mV in the low current-density range by increasing of the Pt-Ru loading amount at an anode electrode, the Pt-Ru loading amount should be doubled.

In the previous study,<sup>29</sup> Pt utilization of a cathode electrode in H<sub>2</sub>/O<sub>2</sub> fuel cell was measured by in situ cyclic voltammetry (CV). However, it is known that hydrogen adsorption-desorption wave pattern and peak potential on Pt-Ru catalyst were changed, compared with on Pt catalyst, for the effect of Ru particles.<sup>30,31</sup> Therefore, it is difficult to apply in-situ CV to Pt-Ru catalyst of an anode electrode in DMFC. In this study, the catalyst utilization was evaluated by comparing the fuel-cell performances consisting of two different catalyst loading amount ca. 1.0 mg cm<sup>-2</sup> and ca. 2.0 mg cm<sup>-2</sup> in Fig. 9.

As indicated in Fig. 9, the catalyst utilization was apparently found to be doubled by grafting of methylsulfonic acid groups onto Pt-Ru/Ketjenblack. We can say that the increase of the catalyst utilization was due to the extending of three-phase boundary reaction area, especially in the primary pores that the catalyst area could not utilize electrochemically when using the conventional method. However, the proton conduction process would be the rate-determining step in the partial area of the three-phase boundary reaction area formed around the grafted methylsulfonic acid groups, because the proton conduction between grafted methylsulfonic acid groups was assumed to be lower than in Nafion ionomer due to the

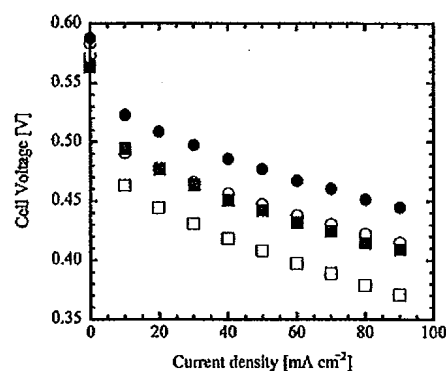


Figure 9. Current-voltage curves at the low current-density range (0–100 mA cm<sup>-2</sup>) of the MBAs made by grafted (■) and nongrafted (□) Pt-Ru/Ketjenblack in the anode Pt-Ru loading amount ca. 1.0 mg cm<sup>-2</sup> and by grafted (●) and nongrafted (○) Pt-Ru/Ketjenblack in the anode Pt-Ru loading amount ca. 2.0 mg cm<sup>-2</sup>. The grafting condition is the same as for sample 1 shown in Table I. Operating conditions: cell temperature 50°C; atmospheric pressure; fuel 2.5 mol L<sup>-1</sup> methanol solution.

low mobility of short grafted chains of methylsulfonic acid groups. It can be concluded that the catalyst area utilized as three-phase boundary reaction area would be enhanced more than twice by grafting of methylsulfonic acid groups onto Pt-Ru/Ketjenblack.

From the above results, it was shown that grafted methylsulfonic acid groups in the pores of catalyst-supported carbons acted as the proton-conducting agent and, therefore, in accordance with the concept of this study illustrated in Fig. 2, the three-phase boundary as an electrochemically active area was formed around the grafted methylsulfonic acid groups, especially in the primary pores, and the methanol oxidation reaction rate was enhanced. Moreover, it was also concluded that mass transport problems were not caused by introducing grafted methylsulfonic acid groups into the pores of the catalyst-supported carbons.

We have obtained an extremely high cell performance by using the MEA made by grafted Pt-Ru/Ketjenblack (sample 3) in addition to an improvement of the macroscale electrode fabrication process. Figure 10 shows that the maximum power density of the MEA was 87 mW cm<sup>-2</sup> by using grafted catalyst-supported carbons for the

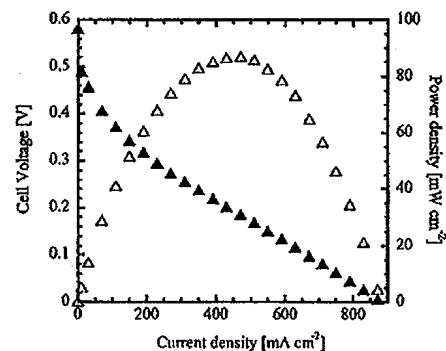


Figure 10. Current-voltage and current-power curves of the MEA made by grafted Pt-Ru/Ketjenblack ((▲), (Δ)). The grafting condition is the same as for sample 3 shown in Table I. Operating conditions: cell temperature 50°C; atmospheric pressure; fuel 2.5 mol L<sup>-1</sup> methanol solution; anode Pt-Ru loading amount ca. 0.7 mg cm<sup>-2</sup>.



DMFC anode electrode in the low Pt-Ru loading amount of ca.  $0.7 \text{ mg cm}^{-2}$  (Pt loading amount: ca.  $0.5 \text{ mg cm}^{-2}$ ) at  $50^\circ\text{C}$  under atmospheric pressure.

### Conclusions

A new approach to the development of a catalyst layer for a DMFC application has been proposed. This is achieved by introducing grafted methylsulfonic acid groups onto catalyst-supported carbons. The following conclusions can be drawn from the above investigation.

1. Grafted methylsulfonic acid groups have been successfully introduced to the pores of catalyst-supported carbons using our technique and the chemical connection between the grafted methylsulfonic acid groups and the surface of catalyst-supported carbons was considered to be stable up to around  $380^\circ\text{C}$ .
2. Grafted methylsulfonic acid groups could be introduced onto catalyst-supported carbons up to ca. 10 vol % (the volume percentage per the primary pore volume) using our technique. From mercury intrusion porosimetry, we also confirmed that the grafted methylsulfonic acid groups decreased the primary pore volume. Furthermore, bubble point tests showed no significant change in the secondary pore size distribution (which has an effect on the mass transfer process) of the anode electrode made by grafted catalyst-supported carbons, compared with that of the anode electrode made by nongrafted catalyst-supported carbons.
3. The MEA using the anode electrode made by grafted catalyst-supported carbons showed superior cell performance to that made by nongrafted catalyst-supported carbons. The maximum power density of  $90 \text{ mW cm}^{-2}$  was obtained by using grafted catalyst-supported carbons for the DMFC anode electrode in the low Pt-Ru loading amount of ca.  $1.0 \text{ mg cm}^{-2}$  (Pt loading amount: ca.  $0.7 \text{ mg cm}^{-2}$ ) at  $50^\circ\text{C}$  under atmospheric pressure. We found that by grafting methylsulfonic acid groups onto catalyst-supported carbons, additional mass transport problems were not caused in the fuel cell tests in the high current-density range because the chain length of the grafted methylsulfonic acid groups was far shorter than that of ATBS polymer. Furthermore, we also confirmed that the electrochemically active catalyst area was greatly increased, especially in the primary pores, by grafting the methylsulfonic acid groups onto catalyst-supported carbons and that the methanol oxidation reaction rate was enhanced because the grafted methylsulfonic acid groups acted as proton-conducting agents, especially in the primary pores that the catalyst area could not utilize electrochemically when using the conventional method. Moreover, we obtained extremely high cell performance by using MEA made by grafted catalyst-supported carbons in addition to an improvement in the macroscale electrode fabrication process. The maximum power density of the MEA was  $87 \text{ mW cm}^{-2}$  in the DMFC test in the low Pt-Ru loading amount of ca.  $0.7 \text{ mg cm}^{-2}$  (Pt loading amount: ca.  $0.5 \text{ mg cm}^{-2}$ ) at  $50^\circ\text{C}$  under atmospheric pressure.

As mentioned above, we showed the effectiveness of nanoscale morphological control using the novel electrode fabrication method.

We also suggested that the electrode fabrication method results in a significant reduction of the catalyst loading amount that is simultaneously accompanied by a higher cell performance, compared with the conventional method. Moreover, we consider that the grafting of methylsulfonic acid groups onto catalyst-supported carbons can be applied to cathode electrodes in liquid-fed DMFCs and in  $\text{H}_2/\text{O}_2$ -PEFCs, as well as anode electrodes in liquid-fed DMFCs.

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